From:

Mire, June

To:

chen.isaac@epa.gov; shaikh.taimur@epa.gov

Cc:

Kuehn, Rob (robert.kuehn@shell.com); gail korenaga (gkorenaga@chevron.com); Smith, Joe P

Subject:

OOC Mud and Produced Water Characterization Study - Revised SAP/QAPP

Date:

Monday, March 24, 2014 11:34:11 AM

### Hi, Isaac and Taimur,

I am following up on our February 25, 2014, conference call in which we discussed changes to the protocol for analyzing water based mud samples for the Mud and Produced Water Characterization Study in response to GMG290000. The attached file contains the complete revised SAP/QAPP. In addition to updating the text to reflect changes to the analytical protocols, we have included a new section (Appendix D) that provides the technical and logistical rationale for the revised plan.

Please let me know if you have any questions or comments on this revised SAP/QAPP. I am also sending you a hard copy by registered mail.

Thanks,

June

June B. Mire, Ph.D. | Senior Ecologist, Project Manager
Direct: 504.834.6276 | Cell: 504.273.9186 | june.mire@tetratech.com
1408 Pasadena Avenue | Metairie, LA 70001

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	: :



March 24, 2014

By electronic mail to:

chen.isaac@epa.gov; shaikh.taimur@epa.gov

Re:

Sampling and Analysis Plan, including Quality Assurance Project Plan and

Sampling Procedures; Revision 01

Joint Industry Project (JIP) Mud and Produced Water Characterization Study to Meet Requirements of the NPDES Permit for the Western and Central Gulf of Mexico Outer

Continental Shelf (GMG 290000)

Dear Mr. Chen:

On behalf of the Offshore Operator Committee, we are submitting Revision 01 of the Sampling and Analysis Plan (SAP) and Quality Assurance Project Plan (QAPP) for the above-referenced project. As we discussed with you on February 25, 2014, we have modified the approach to analyzing water based mud samples to reflect the availability of aqueous phase in some samples. We are now analyzing all water based mud samples for total metals, hexavalent chromium, and cyanide. We are analyzing dissolved constituents in water based mud samples that yield adequate aqueous phase. We have deprioritized analysis of dissolved cyanide, as agreed.

The attached file contains the complete Revision 01 of the SAP/QAPP. Please note that a new appendix has been added to the SAP. Appendix D, Water Based Mud Characterization, provides the technical and logistical rationale for the revised analytical plan.

To date we have collected and analyzed 47 water based mud samples from 16 different lease areas. We are in the process of analyzing total constituents in the archived water based mud samples collected earlier in the study; all constituents except mercury and cyanide are within holding times. Samples collected since our conversation on February 25, 2014 have been analyzed as described in the attached SAP/QAPP. If we do not hear from you by April 15, 2014, we will assume your concurrence with this revised SAP/QAPP.

Please do not hesitate to call me at (504) 834-6276 if you would like to discuss this revision or other aspects of the study.

June B. Mire, Ph.D.

SineBorgire

Tetra Tech Project Manager

Robert H. Holmes

Tetra Tech Program Manager, Oil & Gas

Robert H. Holmes

Cc: OOC Core Team

Enclosure

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#### SAMPLING AND ANALYSIS PLAN (Revision 01)

# MUD AND PRODUCED WATER CHARACTERIZATION STUDY (MPWCS) TO MEET REQUIREMENTS OF THE NATIONAL POLLUTANT DISCHARGE ELIMINATION SYSTEM (NPDES) PERMIT WESTERN AND CENTRAL GULF OF MEXICO OUTER CONTINENTAL SHELF (OCS) NPDES PERMIT No.: GMG290000

#### Prepared for

# OFFSHORE OPERATORS COMMITTEE (OOC) ENVIRONMENTAL SUBCOMMITTEE

Date Prepared:

OOC Point of Contact:

Telephone No.:

Prepared by:

Tetra Tech Project Manager:

Telephone No.:

March 2014

Robert Kuehn

(504) 425-7693

Tetra Tech, Inc.

June Mire, Ph.D.

(504) 273-9186

Prepared by Jessica Vickers

Tetra Tech Chemist

Reviewed by Jim Collins

Tetra Tech Task Manager

Reviewed by

John Schendel

Tetra Tech Quality Assurance Officer

Approved by

June Mire, Ph.D.

Tetra Tech Project

Manager

Approved by Min Huang

OOC Analytical Subteam Lead

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#### 1.0 INTRODUCTION

The Offshore Operators Committee (OOC) directed Tetra Tech, Inc. (Tetra Tech) to prepare a sampling and analysis plan (SAP) for the Mud and Produced Water Characterization Study (MPWCS) for the Western and Central Gulf of Mexico Outer Continental Shelf (OCS) area (National Pollutant Discharge Elimination System [NPDES] Permit No. GMG290000). The purpose of the SAP is to specify the type, number, and location of samples to be collected during MPWCS activities, as well as the sampling methodology to be followed.

All activities and procedures discussed and described in this SAP will be conducted in accordance with the approved Quality Assurance Project Plan (QAPP), which is consistent with the Tetra Tech Quality Management Plan (Reference [Ref.] 1). Tetra Tech will perform activities in accordance with the prescribed guidance and informational documents listed below to further ensure that all data quality objectives (DQO) are met.

- Environmental Protection Agency (EPA) Test Methods for Evaluating Solid Waste,
   Fourth Edition, Including Updated, I through IVB, February 2007 (SW-846) Methods
   6020A (dissolved metals), 7470A (dissolved mercury), 7196A (dissolved hexavalent chromium), and 9014 (dissolved cyanide) (Ref. 2)
- EPA Method 218.6: Determination of Dissolved Hexavalent Chromium in Drinking Water, Groundwater, and Industrial Wastewater Effluents by Ion Chromatography, Revision 3.3, 1994 (Ref. 3)
- EPA National Functional Guidelines (NFG) for Inorganic Superfund Data Review,
   EPA540-R-10-011, January 2010 (Ref. 4)
- EPA Guidance on Systematic Planning Using the Data Quality Objectives (DQO)
   Process, EPA QA/G-4, February 2006 (Ref. 5)
- EPA Region 6, Fact Sheet and Supplemental Information for the Proposed
  Reissuance of the NPDES General Permit for New and Existing Sources in the
  Offshore Subcategory for the Western Portion of the Outer Continental Shelf of the
  Gulf of Mexico (GMG290000), December 2012 (Ref. 8)
- EPA Region 6, The NPDES General Permit for New and Existing Sources and New Discharges in the Offshore Subcategory of the Oil and Gas Extraction Point Source Category for the Western Portion of the Outer Continental Shelf of the Gulf Of Mexico (GMG290000), 2012 (Ref. 9)

These guidance documents specifically apply to sampling locations, sample types, sampling procedures, use of data, data types, field quality assurance and quality control (QA/QC) samples, sample analyses, and data validation. The following web sites were used to provide information on the spatial distribution of the study region:



- Google Earth. Distance check from Central to Western portion of the Gulf of Mexico. May 2013. (Ref. 6)
- NOAA Ocean Explorer: Expedition to the Deep Slope.
   <a href="http://oceanexplorer.noaa.gov/explorations/o6mexico/background/oil/media/platforms">http://oceanexplorer.noaa.gov/explorations/o6mexico/background/oil/media/platforms</a> 600.htmlMay 2013 (Ref. 7)

The primary purpose of the MPWCS is to meet EPA permit requirements that include a characterization study of water based mud (WBM) and produced water (PW) for the express purpose of having "more area-specific data for future evaluations;" and to collect data in areas to characterize representative discharges from wells in the OCS area. Activities for the MPWCS will include the following:

- Identify sample locations using geographic information system (GIS) and a hierarchical optimization system
- Select produced water sample locations to ensure that the entire data set will be representative of overall offshore production
- Collect samples to determine the soluble concentration of arsenic, cadmium, copper, cyanide, hexavalent chromium, lead, mercury, nickel, selenium, silver, and zinc in WBM and PW

The remainder of this SAP for MPWCS activities in the OCS area is organized as follows:

- Section 2.0 presents background information, including the site description and environmental setting, and regulatory background.
- Section 3.0 summarizes proposed field sampling activities, including descriptions of sampling methods.
- Section 4.0 describes the data quality objectives.
- Section 5.0 describes the analytical methodology.
- Section 6.0 presents the project personnel and their responsibilities.
- Section 7.0 provides a list of references consulted.
- Appendix A provides sampling procedures and reference checklists.
- Appendix B provides the tables.
- Appendix C provides the quality assurance project plan (QAPP).
- Appendix D discusses the technical approach to characterizing water based mud samples that do not yield water when centrifuged.



#### 2.0 SITE BACKGROUND

This section describes the site and environmental setting, discusses past operations, and summarizes previous investigations for the OCS area.

#### 2.1 SITE DESCRIPTION AND ENVIRONMENTAL SETTING

The Western and Central OCS area is located on the southern boundary of the United States and extends from Alabama to the Texas coastline, a distance of approximately 630 miles (Refs. 6; 7). The central and western areas of the Gulf of Mexico have nearly 4,000 active oil and gas platforms (Ref. 7).

#### 2.2 REGULATORY BACKGROUND

On April 3, 1981, the EPA published NPDES permit TX008562. The permit authorized discharges from facilities located seaward of the outer boundary of the territorial seas off Louisiana and Texas, an area commonly known as the Outer Continental Shelf. Permit restrictions limited oil and grease releases to 72 milligrams per liter (mg/L) a day; prohibited the discharge of oil based drilling fluids; imposed a limit of no free oil for drilling fluids, drill cuttings, deck drainage and well treatment fluids; and imposed a 1 mg/L residual chlorine limit for sanitary waste water (Ref. 8).

The permit was reissued on July 9, 1986 by EPA Region 6 and EPA Region 4 as permit number GMG280000. The permit prohibited discharge of oil based drilling fluids, oil contaminated drilling fluids, drilling fluids containing diesel oil, and drill cuttings generated using oil based drilling fluids. The permit also included new limits on suspended particulate phase toxicity in drilling fluids, on the drilling fluid discharge rate near areas of biological concerns, and on free oil drilling and drill cuttings. On November 19, 1992, the NPDES Permit was reissued by EPA Region 6 as GMG290000. New limits were included in the reissuance for produced water toxicity, for cadmium and mercury in stock barite, and prohibition on discharge of drilling fluids containing mineral oil (Ref. 8).

NPDES Permit GMG290000 underwent additional modifications over the years. A summary of the revisions is included below (Ref. 8):

- **December 3, 1993:** Offshore subcategory effluent limitations guidelines and more accurate calculations of produced water critical dilutions.
- August 9, 1996: New Sources combined into the permit.



- November 2, 1998: New discharges of saltwater and freshwater (biocides and corrosion inhibitors); maximum discharge rate for produced water removed; and critical dilutions required for produced water toxicity limit updated.
- December 18, 2001: New discharges associated with synthetic based drilling fluids and additional monitoring requirements for hydrostatic testing of existing piping and pipelines.
- October 7, 2004: Produced watering monitoring requirements for facilities in hypoxic zone; discharge prohibitions at National Marine Sanctuaries clarified; variability factor for determining compliance with the permit's limits for sediment toxicity and biodegradation removed; allowance for blending of compliant synthetic base fluids in drilling fluids added; and fourteen day advanced notification removed.
- June 7, 2007: Requirements to comply with new cooling water intake structure regulations added; sub-lethal effects for whole effluent toxicity testing to be measured; and new test methods allowed for monitoring cadmium and mercury in stock barite.

On October 1, 2012, the current reissued NPDES Permit GMG290000 went into effect and covers lease areas and discharges in the central and western portions of the Gulf of Mexico (Ref. 9).

#### 3.0 PROPOSED SAMPLING PLAN

This SAP describes the samples to be collected; sampling methodologies; applicable holding times and record keeping; analytical techniques and target detection limits; as well as the platforms and rigs to be sampled. Sampling will be conducted, and QA/QC samples will be collected, in accordance with procedures detailed in the Sampling Procedures Reference Checklists found in Appendix A. Sample holding times will be minimized as much as possible by close coordination with the operators so that samples can be transported on supply vessels and helicopters to the nearest shore-based support facility.

The personnel that will collect the samples are the same personnel who currently collect samples under the NPDES monitoring programs on the rigs/platforms. These personnel on the rigs/platforms will receive training on the sampling procedures via a training video that will be made available to them prior to sampling. The Sampling Procedures Reference Checklists will be emailed to the sampling personnel and supervisors prior to sampling, and the Tetra Tech chemist will set up a presampling conference with the personnel to verify that the training video has been viewed and to review the procedures. If the operators have access to a phone, the Tetra Tech chemist will be available to address any questions that may arise during sampling. If phone contact during sampling is not available, the sampling personnel will call the Tetra Tech chemist as soon as reasonably possible after sampling to debrief on the sample collection.

The sampling personnel will be required to check off the steps enumerated in the Sampling Procedures Reference Checklists in Appendix A, and to sign and date the checklists to verify that the procedures were followed. Because EPA Region 6 field sampling procedures were not available, the Sampling Procedures Reference Checklists were prepared by referencing the appropriate EPA Region 4, Science and Ecosystem Support Division (SESD), Field Branches Quality System and Technical Procedures (Refs. 10 through 15). Table 1 in Appendix B outlines the numbers and types of samples proposed, as well as sampling locations. Table 2 in Appendix B summarizes the QA/QC samples to be collected during field sampling activities. The analytical methodology is described in Section 5.0 of this SAP.

#### 3.1 WATER BASED MUD SAMPLING

#### Sampling Design

The Western and Central OCS consists of 69 designated surface areas, each of which is divided into numerous lease blocks (a geographical area of approximately 9 square miles [5,760 acres]).

The ideal sampling design would include ten WBM samples from each of 10 different blocks within each State- or Bureau of Ocean Energy Management-designated surface area. However, WBM samples must be collected during active drilling, so actual sample collection will necessarily be opportunistic. Participating operators will identify where drilling will occur during the sample collection phase of this project. Drilling plans and locations are proprietary and cannot be presented in this sampling plan. Tetra Tech will work with the participating operators to obtain proposed drilling schedules, which will allow for optimization of the sampling design and ensure that representative samples are collected.

To the extent practicable, Tetra Tech will have the operators collect a WBM sample from each active drilling operation that satisfies the spatial criteria of the MPWCS. The goal is to collect a total of 10 WBM samples from each of 10 different blocks within each designated surface area. The schedule and locations must be flexible to accommodate unexpected changes in drilling activities. Estimated sample collection locations based on drilling activities between 2009 and 2012 are shown in Table 3 for illustration. Actual sample locations will be determined by drilling activity during the study period.

#### Sampling Procedure

The rig/platform personnel will collect WBM samples from wells during drilling activities. The WBM samples will be collected in accordance with the procedures outlined in the Sampling Procedure and Checklist (Appendix A) and sent to ALS Group (ALS) in Houston, Texas, a Tetra Tech-procured laboratory. If the offshore support location for the rig/platform is the Port of Galveston, ALS will pick up the sample cooler and transport it to their laboratory. If an alternate offshore support location is used, the cooler will be shipped by Federal Express to the laboratory. Shipping instructions are included in the Sampling Procedure and Checklist (Appendix A). Upon receipt of the WBM sample, the laboratory will homogenize the sample using procedures described in Methods for Collection, Storage, and Manipulation of Sediments for Chemical and Toxicological Analyses: Technical Manual (REF 17). A portion of the homogenized sample will be analyzed for total metals (arsenic, cadmium, copper, lead, mercury, nickel, selenium, silver, and zinc); cyanide; and hexavalent chromium using



methods suitable for either solids or water (depending on the consistency of the particular sample). The lab will centrifuge another portion of the homogenized WBM sample and decant available water to filter and analyze the sample for dissolved phase metals (arsenic, cadmium, copper, lead, mercury, nickel, selenium, silver, and zinc); dissolved hexavalent chromium; and dissolved cyanide.

As discussed with US EPA Region 6 personnel on February 25, 2014, some WBM samples collected to date have yielded very little water when centrifuged (see Appendix D for a discussion of the steps taken to extract water from WBM samples and summary notes of the February 25, 2014 meeting). If a WBM sample does not yield enough water to analyze all of the parameters listed above, the lab will analyze as many parameters as possible on each sample, in the following order of priority: metals, hexavalent chromium, cyanide. Table 1 in Appendix B outlines the numbers, types, and analytical methods for WBM samples. A discussion of the relative priority of cyanide analysis is in Appendix D.

In addition, water based muds collected under the original SAP (prior to this revision) have been archived in the lab. These samples will be analyzed for total constituents as described above, with the exception of mercury and cyanide in some of the older samples that have exceeded the holding time.

The spud mud used for drilling the top hole before the risers are in place can be characterized as "miscellaneous discharge" or as "drilling discharge" and is not representative of typical drilling mud because it usually contains bentonite clay (and sometimes barite), which is not implicated in toxicity. Additionally, because this mud is discharged directly to the sea floor, it would be impractical to collect quality-control samples as "used" mud for this study. This characterization study proposes to first sample returned "used" mud (after riser installation). If that is impracticable (due to the operator switching to synthetic mud after riser installation), the study proposes to take "unused" spud mud from the active pits rather than attempting to sample "used" mud from the seafloor to characterize this portion of drilling discharges.

#### 3.2 PRODUCED WATER SAMPLING

Samples of produced water will be collected from offshore production platforms of participating operators. Participating operators currently control active produced water outfalls in 28 different surface areas (Table 4 in Appendix B). PW samples will be collected using a stratified random sampling approach based on the geographic location (surface area/block) and a representative, weighted distribution of operators. Outfalls will be selected for sampling to achieve the desired spatial distribution specified in the permit, with no more than 10 samples from each surface area and no more than one unique sample from each block. To the extent practicable, outfalls will be selected to ensure representation of all participating operators. In surface areas with more than 10 active blocks containing produced water outfalls controlled by participating operators, sample locations were randomly selected using a grid and random number generator. Proposed sample locations are shown in Table 4 in Appendix B.

The PW samples will be collected in accordance with the procedures outlined in the Sampling Procedure and Checklist (Appendix A) and sent to ALS in Houston, Texas, a Tetra Tech-procured laboratory. If the offshore support location for the rig/platform is the Port of Galveston, ALS will pick up the sample cooler and transport to laboratory. If an alternate offshore support location is used, the cooler will be shipped by Federal Express to the laboratory. Shipping instructions are included in the Sampling Procedure and Checklist (Appendix A). Upon receipt of the PW sample, the laboratory will analyze the sample for dissolved phase arsenic, cadmium, copper, cyanide, hexavalent chromium, lead, mercury, nickel, selenium, silver, and zinc. Table 1 in Appendix B outlines the numbers, types, and analytical methods for PW samples.

#### 4.0 DATA QUALITY OBJECTIVES

Data Quality Objectives (DQOs) for the MPWCS are discussed in the Quality Assurance Project Plan (QAPP) included as Appendix C to this SAP. The QAPP was developed following EPA's Requirements for Quality Assurance Project Plans, EPA QA/R-5, EPA/240/B-01/003, reissued May 2006 (Ref. 15). DQOs were established to define the quantity and quality of the data to be collected in support of the MPWCS objectives.

Sampling and laboratory analysis will be conducted to provide information for comparing dissolved pollutant concentrations of the samples to EPA Ambient Water Quality Criteria for saltwater (Ref.16). Other uses of the study results may include EPA conducting reasonable potential analyses of discharge concentrations to exceed ambient water quality criteria, possible refinement of the NPDES permit and to inform future Ocean Discharge Criteria Evaluations, as well as to characterize representative discharges from the wells in the OCS area.

QA/QC samples will be collected during the sampling event to check for variations with sample collection, sample handling, and laboratory analysis. The QA/QC samples to be collected and their proposed frequencies are summarized in Table 2 of Appendix B.

Tetra Tech will assess the analytical results for initial acceptance during a Stage 4 validation of the samples that will determine the usability of the data. Any rejected data and the reasons for rejection will be summarized in the data quality assessment (DQA) report.



#### 5.0 ANALYTICAL METHODOLOGY

WBM and PW samples will be submitted to ALS in Houston, Texas, a Tetra Tech-procured laboratory. Table 1 of Appendix B presents the analyses to be performed for WBM and PW samples. Table 5 of Appendix B presents the analytical methodology for each sample matrix, including required sample containers and preservatives. The analytical parameters for WBM and PW samples are described below:

- Selected dissolved metals (arsenic, cadmium, copper, lead, nickel, selenium, silver, and zinc) in PW and WBM and total metals (in WBM only) will be analyzed by EPA Test Methods for Evaluating Solid Waste, Fourth Edition, Including Updated, I through IVB, February 2007 (SW-846) Method 6020A (Ref. 2).
- Dissolved mercury will be analyzed by SW-846 Method 7470A and total mercury in WBM by SW-846 Method 7471B (Ref. 2).
- Dissolved and total cyanide will be analyzed by SW-846 Method 9014 (Ref. 2).
- Dissolved and total hexavalent chromium will be analyzed by SW-846 7196A (for WBM samples) (Ref. 2).
- Dissolved hexavalent chromium will be analyzed by EPA Method 218.6 (for PW samples) (Ref. 3).

Additionally, for the first 20 PW samples collected, an unfiltered and unpreserved sample container will be submitted to the laboratory. This sample aliquot will be filtered by the laboratory upon receipt, preserved with the buffer solution, and analyzed for dissolved hexavalent chromium by EPA Method 218.6.

Any variations in the analytical methodology will be specified in the monthly summary reports submitted to the OOC Steering Committee, as well as the DQA, and final report.

Data validation of the analytical data packages will be conducted by Tetra Tech. A Stage 4 data validation will be conducted in accordance with the EPA NFGs for Inorganic Superfund Data Review, EPA540-R-10-011, January 2010 (Ref. 4); as well as the associated analytical methods. The data packages will also be reviewed to determine whether any data should be rejected and whether any data qualifiers assigned during the validation process affect the usability of the data as defined in Section 1.5 of the QAPP (see Appendix C).



#### 6.0 PROJECT PERSONNEL

Anticipated team members and their responsibilities are as follows:

- June Mire, PhD Project Manager
- Jerry Neff; Randy Bassett, PhD; and Len Nelms, PhD Scientific Advisors
- Matthew Soltis, CIH, CSP and John Schendel, PhD Specialty Services
- Jessica Vickers Laboratory/Analytical/Data Quality Leader
- Jim Collins; Theodore Donn, Jr., PhD; Blaine Snyder; Randy Mayer; and Bryan Vasser Task Leaders

Additional team members will be determined prior to initiation of sample collection.



#### 7.0 REFERENCES (Continued)

- 1. Tetra Tech EM Inc. (Tetra Tech), Quality Management Plan, Revision 2. November 2009.
- 2. EPA. Test Methods for Evaluating Solid Waste, Fourth Edition, Including Updated, I through IVB, February 2007 (SW-846) Methods 6020A, 7470A, 7196A, and 9014. February 2007.
- EPA Method 218.6: Determination of Dissolved Hexavalent Chromium in Drinking Water, Groundwater, and Industrial Wastewater Effluents by Ion Chromatography, Revision 3.3, 1994.
- 4. EPA. CLP National Functional Guidelines for Inorganic Superfund Data Review, EPA540-R-10-011. January 2010.
- 5. EPA. Guidance on Systematic Planning Using the Data Quality Objectives Process, EPA QA/G-4. February 2006. Accessed on-line at <a href="http://www.epa.gov/quality/qs-docs/g4-final.pdf">http://www.epa.gov/quality/qs-docs/g4-final.pdf</a>.
- 6. Google Earth. Distance check from Central to Western portion of the Gulf of Mexico. May 2013.
- NOAA. NOAA Ocean Explorer: Expedition to the Deep Slope. <a href="http://oceanexplorer.noaa.gov/explorations/o6mexico/background/oil/media/platforms\_600.htm">http://oceanexplorer.noaa.gov/explorations/o6mexico/background/oil/media/platforms\_600.htm</a>
   <a href="http://oceanexplorer.noaa.gov/explorations/o6mexico/background/oil/media/platforms\_600.htm">http://oceanexplorations/o6mexico/background/oil/media/platforms\_600.htm</a>
   <a href="http://oceanexplorer.noaa.gov/explorations/o6mexico/background/oil/media/platforms\_600.htm">http://oceanexplorations/o6mexico/background/oil/media/platforms\_600.htm</a>
   <a href
- 8. EPA. EPA Region 6, Fact Sheet and Supplemental Information for the Proposed Reissuance of the NPDES General Permit for New and Existing Sources in the Offshore Subcategory for the Western Portion of the Outer Continental Shelf of the Gulf of Mexico (GMG290000), December 2012.
- EPA. EPA Region 6, The NPDES General Permit for New and Existing Sources and New Discharges in the Offshore Subcategory of the Oil and Gas Extraction Point Source Category for the Western Portion of the Outer Continental Shelf of the Gulf Of Mexico (GMG290000), 2012.
- 10. U.S. Environmental Protection Agency (EPA), Region 4 Science and Ecosystem Support Division (SESD) Field Branches Quality System and Technical Procedure for Waste Sampling. January 2013. Accessed on-line at <a href="http://www.epa.gov/region4/sesd/fbqstp/Waste-Sampling.pdf">http://www.epa.gov/region4/sesd/fbqstp/Waste-Sampling.pdf</a>.
- EPA, Region 4 SESD Field Branches Quality System and Technical Procedure for Wastewater Sampling. February 2013. Accessed on-line at <a href="http://www.epa.gov/region4/sesd/fbqstp/Wastewater-Sampling.pdf">http://www.epa.gov/region4/sesd/fbqstp/Wastewater-Sampling.pdf</a>.
- 12. EPA, Region 4 SESD Field Branches Quality System and Technical Procedure for Field Sampling Quality Control. February 2013. Accessed on-line at <a href="http://www.epa.gov/region4/sesd/fbqstp/Field-Sampling-Quality-Control.pdf">http://www.epa.gov/region4/sesd/fbqstp/Field-Sampling-Quality-Control.pdf</a>.
- 13. EPA, Region 4 SESD Field Branches Quality System and Technical Procedure for Sample and Evidence Management. January 2013. Accessed on-line at <a href="http://www.epa.gov/region4/sesd/fbqstp/Sample-and-Evidence-Management.pdf">http://www.epa.gov/region4/sesd/fbqstp/Sample-and-Evidence-Management.pdf</a>.
- 14. EPA, Region 4 SESD Field Branches Quality System and Technical Procedure for Packing, Marking, Labeling, and Shipping of Environmental and Waste Samples. April 2011. Accessed on-line <a href="http://www.epa.gov/region4/sesd/fbqstp/Shipping-Environmental-and-Waste-Samples.pdf">http://www.epa.gov/region4/sesd/fbqstp/Shipping-Environmental-and-Waste-Samples.pdf</a>.



# 7.0 REFERENCES (Continued)

- 15. EPA. EPA Requirements for Quality Assurance Project Plans, EPA QA/R-5, EPA/240/B-01/003, Reissued May 2006.
- 16. EPA. EPA Ambient Water Quality Criteria for saltwater. Accessed on-line <a href="http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm#appendxa">http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm#appendxa</a>.
- 17. EPA. Methods for Collection, Storage, and Manipulation of Sediments for Chemical and Toxicological Analyses: Technical Manual, EPA/823/B-01/002. Office of Water. http://epa.gov/waterscience/cs/library/collection.html. 2001



# **APPENDIX A**

# SAMPLING PROCEDURES AND CHECKLISTS

(Twelve Pages)



#### WATER BASED MUD SAMPLING PROCEDURE (2 pages)

Contact Jessica Vickers at Jessica. Vickers@tetratech.com: (678) 983-6655.

This document details the process covered in the training video. You should watch the training video no more than <u>five</u> days before you collect the samples. We will email a copy of this procedure to you before we send you the Sampling Kit. The Sampling Kit will contain a <u>checklist</u> for this sampling procedure. Use both this procedure and the checklist to guide you during sampling. When finished, sign and date the checklist **and include it with the sample shipment**.

- I. SAMPLING KIT The Sampling Kit will include *one cooler*. Please open the cooler and confirm that it contains the following items:
  - Checklist (to be completed and returned to us)
  - Chain-of-custody (COC) form (see Attachment 1)
  - Custody seals (2)
  - Large garbage bags (2)
  - Sampling gloves (5 pair)
  - Paper towels
  - Pre-labeled wide-mouth plastic jars (2 per sample [see Attachment 2])
  - Ziploc bags (1 for COC form and checklist, and 1 for each sample container)
  - Roll of clear plastic tape
  - Pre-filled-out Federal Express shipping label
  - A sharpie marker

#### II. PRE-SAMPLING INSTRUCTIONS

(Note: Before sample collection, have enough ice on hand to fill the cooler.)

- Place the sample containers and other supplies in a clean location.
- Place one large garbage bag inside the other one to form a double-layered garbage bag. Put the
  double-layered garbage bags inside the cooler, with their openings facing upward.
- Fill the double-layered garbage bag inside the cooler almost all the way with ice. Leave enough room for the sample containers to also fit inside.
- Write the current date, time, and your initials with a sharple on the label of each sample jar.
- Write the current date and time on each row where a sample is listed on the COC form, using a sharpie (date and time on COC should match the sample container labels). Print and sign your name in the space provided for "Sampler(s)." Sign and write the current date and time in the "Relinquished by:" block.
- Sign and write the current date on each custody seal, using a sharpie

NOTE: WBM samples should be collected from the returned mud from the well borehole during riser installation. If this is not possible because the WBM will not be used after riser installation, WBM from an active pit (with mud discharge on the seafloor) will be collected instead. *Make notes on the checklist to show where the sample was collected*.

[Continued on page 2]



#### III. SAMPLE COLLECTION

- If some of the *labeled* sample containers have a name ending in "-DUP", set those containers aside along with one of the *unlabeled* 1-gallon plastic bottles.
- Place the *labeled* sample containers without the "-DUP" ending in a convenient place for filling them.
- Put on a new, unused pair of gloves.
- Fill the sample containers to about 95% full with WBM.
- Clean the top rim and threads of the sample container with a paper towel. Close the sample container and hand tighten the lid.
- For sample containers with a name ending in "-DUP," repeat the sample collection steps. Start by putting on new gloves, and repeat the steps above for all containers labeled "-DUP".
- Note on the checklist where the WBM samples was collected.

#### IV. SAMPLE PACKING

- Put on a new, unused pair of gloves. Replace the glove whenever they are torn or become badly soiled.
- Dry all sample containers with paper towels; check that all lids are tight.
- Place each sample container inside a separate Ziploc bag and securely seal the bag.
- Bury each bagged sample container in the ice (in the double-layered garbage bags in the cooler).
   Make sure the sample bottles are upright and not touching each other or the sides of the cooler.
   Surround each bottle completely with a few inches of ice.
- Top off the garbage bag liner with ice so that sample containers will not move around.
- Take off and dispose of the gloves.
- Carefully pull up on the top edges of the garbage bags above the level of the ice and sample containers.
- Push out the excess air from the *inner* garbage bag as you twist it and tie it into a knot. Then, tape the knot down onto the bag using clear plastic tape.
- Repeat for the outer garbage bag. Tape the knot down onto the bag using clear plastic tape.
- Complete, sign, and date the checklist. Put the signed COC form and checklist in a Ziploc bag, securely seal the bag, and tape the bag to the inside of the cooler lid using clear plastic tape.

#### V. SAMPLE COOLER SHIPPING

- Close the cooler. Affix two signed and dated custody seals across the seam of the lid at
  diagonally opposite corners. Tape the lid of the cooler in two places, covering the custody seals,
  with clear tape.
- Affix the Federal Express shipping label to the top of the cooler; tape down its edges.
- Hand off the sample cooler to the person who will transport it to shore.

# WATER BASED MUD SAMPLING CHECKLIST REV 01 (without duplicates)

Contact Jessica Vickers at Jessica. Vickers@tetratech.com or 678-983-6655 (cell).

This document lists the steps covered in the training video, which should be viewed no more than five (preferably within two) days before the day of sampling. Use the *Water Based Mud Sampling Procedure* to guide you during sampling. Check the boxes on this checklist as you complete each step. When finished, sign and date this checklist at the bottom and include it with the sample shipment. Make sure all highlighted information is filled out.

I.	SAMPLING KIT (Check the box to show that t	ne statement is true.)	
	The sampling kit cooler contained all items I	sted in the SAMPLING KIT Section of the	WBM Sampling Procedure.
II.	DOCUMENTATION INSTRUCTIONS		
	The current date, current time, and your initiate to the sample containers, as indicated in the I		The state of the s
	The current date and time have been written and signature have been written in the highligand your signature have been written in the highlighted DOCUMENTATION INSTRUCTIONS of the control of the contro	hted "Sampler(s)" block on the COC form; ghlighted "Relinquished by:" block on the	and the current date, current time,
	The current date, current time, and your signanticated in the DOCUMENTATION INSTI		New Agent and the state of the
III.	PRE-SAMPLING INSTRUCTIONS		
	The cooler has been set up with double-layer INSTRUCTIONS of the WBM Sampling Pro		PRE-SAMPLING
IV.	SAMPLE COLLECTION		
	New, unused gloves were put on when indicate Procedure, and whenever the glove(s) were to		n of the WBM Sampling
	WBM samples were collected as indicated in	the SAMPLE COLLECTION Section of th	e WBM Sampling Procedure.
	Indicate the location of mud sample by circling	pelow. Add comments as needed to clarify	the sample point and conditions:
	Mud returns via riser from well bore  Active pit	<ul><li>Well depth:</li><li>Mud weight:</li></ul>	
	receive pie	Cool Stop Time:	
V.	SAMPLE PACKING		
	Samples were packed into the cooler and sea <i>Procedure</i> .	ed as indicated in the SAMPLE PACKING	Section of the WBM Sampling
Signat	ture	Date	*
rinte	d Name	Location I	D



# WATER BASED MUD SAMPLING CHECKLIST REV 01 (with duplicates)

Contact Jessica Vickers at Jessica. Vickers@tetratech.com or 678-983-6655 (cell).

This document lists the steps covered in the training video, which should be viewed no more than five (preferably within two) days before the day of sampling. Use the *Water Based Mud Sampling Procedure* to guide you during sampling. Check the boxes on this checklist as you complete each step. When finished, sign and date this checklist at the bottom and include it with the sample shipment. Make sure all highlighted information is filled out.

I.	SAMPLING KIT (Check the box to show that the statement is true.)
	The sampling kit cooler contained all items listed in the SAMPLING KIT Section of the WBM Sampling Procedure.
П.	DOCUMENTATION INSTRUCTIONS
	The current date, current time, and your initials have been written in the appropriate highlighted areas of the labels attached to the sample containers, as indicated in the DOCUMENTATION INSTRUCTIONS of the WBM Sampling Procedure.
	The current date and time have been written on the COC form in the highlighted areas for each sample; your printed name and signature have been written in the highlighted "Sampler(s)" block on the COC form; and the current date, current time, and your signature have been written in the highlighted "Relinquished by:" block on the COC form, as indicated in the DOCUMENTATION INSTRUCTIONS of the WBM Sampling Procedure.
	The current date, current time, and your signature have been written on both custody seals in the highlighted areas as indicated in the DOCUMENTATION INSTRUCTIONS of the WBM Sampling Procedure.
III.	PRE-SAMPLING INSTRUCTIONS
	The cooler has been set up with double-layered garbage bags and ice as indicated in the PRE-SAMPLING INSTRUCTIONS of the WBM Sampling Procedure.
IV.	SAMPLE COLLECTION
	New, unused gloves were put on when indicated in the SAMPLE COLLECTION Section of the WBM Sampling Procedure, and whenever the glove(s) were torn or badly soiled.
	WBM samples were collected as indicated in the SAMPLE COLLECTION Section of the WBM Sampling Procedure.
	Indicate the location of mud sample by circling below. Add comments as needed to clarify the sample point and conditions:
,	Mud returns via riser from well bore  Active pit  Air Cool Start Time:  Comments/Coordinate Verification:  Well depth:  Mud weight:  Air Cool Stop Time:
	For the "-DUP" sample, a new unused pair of gloves was put on and the WBM sample procedures were repeated for the containers labeled "-DUP" as indicated in the SAMPLE COLLECTION Section of the WBM Sampling Procedure.
V.	SAMPLE PACKING
	Samples were packed into the cooler and sealed as indicated in the SAMPLE PACKING Section of the WBM Sampling Procedure.
Signatı	Date
rinted	Name Location ID



# **Attachment 1**

ALS Envi	rommentai		u, Texas 77099 281-530-5656				
Client: Tet	ra Tech-GA		ject: OOC-Water Based Mud				
Sample iD	: MPWCS-WBM	-00)					
Date:	Time:_		_ Collect By:				
Analysis: I	Dissolved Metals,	CN,CR6	Preservative: Neat				
BO Prep'd	on: 6/3/2013						
ALS Enviro	onmental		Texas 77009 31-530-5656				
Client: Tetra	Tech-GA		OOC-Water Based Mud				
Sample ID: 1	MPWCS-WBM-0	201					
Date:	Time :		Collect By:				
Analysis: Di	ssolved Metals,C	N,CR6	Preservative: Neat				
BO Prenid or	r: 6/3/2013		m may pure.				



Cincinnati, Oli +1 513 733 5336 Everett, WA +1 425 356 2600 Fort Collins, CO +1 970 490 1511 Holfand, MI +1 616 399 6070

# Chain of Custody Form

Page \_\_\_

Houston, TX +1 281 530 5656 Middletown, PA +1 717 944 5541

83675

Salt Lake City, UT +1 801 266 7700 York, PA +1 717 505 5280

COC IĎ: Attachment 2 Environmenta! ALS Project Manager: ALS Work Order # **Customer Information** Project Information Parameter/Method Request for Analysis OOC-Water based Mud Purchase Order Project Name Dissowed Metals (6020/7000) As,Cd,Cu,Pb,Nt,Sa,Ag,Zn,Hg В Work Order Project Number Discoived Cyankin (9014) ¢ Company Name Tatra Tech Bill To Company Terra Tech Mesolred Hexavalent Chromius Send Report To Jassica Vickers Invoice Attn Jessica Vickers D 1955 Evergreen Blvd. 1955 Evergreen Blvd. Ė Address Address F 849, 200, Ste. 300 Bldg. 200, Ste. 305 Ġ Odith, GA 30096 Gity/State/Zip Outurh, GA 300/16 City/State/Zip Ĥ (676) 775-3104 (878) 775-3104 Phone Phone. Fax Fax J e-Mail Address e-Mail Address Matrix # Bottles A Hold Sample Description B 0 Nσ. MPWCS-WEM-001 Х Χ Х 2 4 5 6 9 10 Shipment Method Required Turnaround Time: (Check Box) Sampler(s) Please Print & Sign-NO Std 10 MK Days - L ] 5 MK Days Retinguished by Date: Received by: Notes: 10 Day TAT. Received by (Laboratory): Date: Time: Relinquished by: Coeler (O Cooler Tamp. QC Package: (Check One Box Below) Level if Stiff QC TRRP ChickLin TRRP Chucklis Chocked by (Leboratory): Logned by (Laboratory): Timo: Teval A SM938ACTS 6-NaHSO<sub>4</sub> 7-Other 8-4°C 9-5035 Preservative Key: 1-HCl 2-HNO<sub>3</sub> 3-H<sub>2</sub>SO<sub>4</sub> A-NaOH 6-Ne<sub>2</sub>S<sub>2</sub>O<sub>3</sub> Other / EDD \_

Note: 1. Any changes must be made in writing once samples and COC form have been submitted to ALS Environmental.

2. Unless otherwise agreed in a formal contract, services provided by ALS Environmental are expressly limited to the terms and conditions stated on the reverse.

3. The Chain of Custody is a legal document. All information must be completed accurately.

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# PRODUCED WATER SAMPLING PROCEDURE (2 pages)

Contact Jessica Vickers at Jessica. Vickers@tetratech.com: (678) 983-6655.

This document details the process covered in the training video. You should watch the training video no more than <u>five</u> days before you collect the samples. We will email a copy of this procedure to you before we send you the Sampling Kit. The Sampling Kit will contain a <u>checklist</u> for this sampling procedure. Use both this procedure and the checklist to guide you during sampling. When finished, sign and date the checklist **and include it with the sample shipment**.

- > SAMPLING KIT The Sampling Kit will include *one cooler* and *one tote*. Please open the *cooler* and confirm that it contains the following items:
  - Checklist (to be completed and returned to us)
  - Chain-of-custody (COC) form (see Attachment 1)
  - Custody seals (2)
  - Large garbage bags (2)
  - Sampling gloves (5 pair)
  - Paper towels; roll of clear plastic tape; and sharpie marker
  - Pre-labeled plastic bottles (3 per sample: 1 with nitric acid, 1 with sodium hydroxide, and 1 with buffer solution) [Note: there will be an additional unpreserved plastic bottle for the first 20 locations sampled]
  - Unlabeled gallon plastic bottle (1)
  - Ziploc bags (1 for COC form and checklist, and 1 for each sample container)
  - Pre-filled-out Federal Express shipping label

Please open the *tote* and confirm that it contains the following items:

- A pre-assembled peristaltic pump, set up
- Spare lengths of tubing (2) [for the "-DUP" samples]
- Spare 0.45 micron filters (2 to 5)
- Pre-filled-out Federal Express shipping label

#### PRE-SAMPLING INSTRUCTIONS

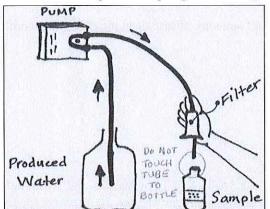
(Note: Before sample collection, have enough ice on hand to fill the cooler.)

- Put the sample containers and other supplies in a clean location.
- Place one large garbage bag inside the other one to form a double-layered garbage bag. Place the double-layered garbage bags inside the cooler, with their openings facing upward.
- Place enough clean, unused ice into the double-layered garbage bag inside the cooler to fill it almost all the way, but leave enough room for the sample containers to also fit inside.
- Write the current date, current time, and your initials with a sharple on the label of each sample bottle.
- Write the current date and time on each row where a sample is listed on the COC form, using a sharpie (Date and time on COC should match the sample container labels). Print and sign your name in the space provided for "Sampler(s)." Sign and write the current date and time in the "Relinquished by:" block.
- Sign and write the current date on each custody seal, using a sharpie.



#### > SAMPLE COLLECTION: (IMPORTANT: You must filter the sample immediately after it is collected.)

- If some of the *labeled* sample containers have a name ending in "-DUP", set those containers aside along with one of the *unlabeled* 1-gallon plastic bottles.
- Place the *labeled* sample containers *without* the "-DUP" ending in a convenient place for filling them.
- Put on a new, unused pair of gloves.
- Remove the peristaltic pump with tubing and filter assembly from the tote and arrange it in a clean location.



- Fill the *unlabeled* sample container to about 95% full with PW. (You have 15 minutes from this point to complete the filtration step and fill the sample bottles.)
- Place the <u>inlet</u> tubing into the PW container and hold the tubing over the opening of a *labeled* sample container (Figure 2).
- Turn on pump and collect filtered water until sample container is about 95% filled. If the filter becomes clogged and the flow slows down too much, turn off the pump, pull the filter off the tubing, and replace it with a new filter. Make sure the new filter is oriented with the direction of flow (arrow pointing toward the container being filled).
- After filling, turn off the pump, clean the top rim and threads of the labeled sample container with a paper towel, and

hand tighten the lid on the sample bottle. Repeat the filtering steps for the other labeled sample containers (without the "-DUP,")

• For sample containers with a name ending in "-DUP," remove the teflon tubing and filter from the pump and replace with the extras sent in your sampling kit tote as shown in Attachment 3. Repeat the sample collection steps, starting with putting on a new unused pair of gloves, for the rest of the sample containers.

#### SAMPLE PACKING

- Put on a new, unused pair of gloves. Replace the gloves whenever they are torn or become badly soiled.
- Dry all sample containers with paper towels; check that all lids are tight.
- Place each sample container inside a separate Ziploc bag and securely seal the bag.
- Bury each bagged sample container in the ice (in the double-layered garbage bags in the cooler). Make sure
  the sample bottles are upright and not touching each other or the sides of the cooler. Surround each bottle
  completely with a few inches of ice.
- Top off the garbage bag liner with ice so that sample containers will not move around.
- Take off and dispose of the gloves.
- Carefully pull the top edges of the garbage bags up above the level of the ice and sample containers.
- Push out the excess air from the *inner* garbage bag as you twist it and tie it into a knot. Then, tape the knot down onto the bag using clear plastic tape.
- Repeat for the *outer* garbage bag. Tape the knot down onto the bag using clear plastic tape.
- Complete, sign, and date the checklist. Put the signed COC form and checklist in a Ziploc bag, securely seal the bag, and tape the bag to the inside of the cooler lid using clear plastic tape.

#### > SAMPLE COOLER AND TOTE SHIPPING

- Close the cooler. Affix two signed and dated custody seals across the seam of the lid at diagonally opposite corners. Tape the lid of the cooler in two places, covering the custody seals, with clear tape.
- Affix the Federal Express shipping label *addressed to ALS* to the top of the cooler; tape down its edges.
- Put the pump, tubing, and all filters (unused and used; with used filters placed inside a sealed Ziploc bag) into the tote. Pack the tote so that the items will not jostle around. Tape the tote closed in two places.
- Affix the Federal Express shipping label *addressed to Tetra Tech* to the top of the tote; tape down its edges.
- Hand off the sample cooler and tote to the person who will transport them to shore.



# PRODUCED WATER SAMPLING CHECKLIST Rev01 (without duplicates)

Contact Jessica Vickers at Jessica. Vickers@tetratech.com or 678-983-6655 (cell).

This document lists the steps covered in the training video, which should be viewed no more than five (preferably within two) days before the day of sampling. Use the *Produced Water Sampling Procedure* to guide you during sampling. Check the boxes on this checklist as you complete each step. When finished, sign and date this checklist at the bottom and include it with the sample shipment. Make sure all highlighted information is filled out.

1.	SAMPLING KIT (Check the box to show that the statement is true.)	
	The sampling kit cooler contained all items listed in the SAMPLING KIT Section of the PW Sampling Procedure.	
	The pump case contained all items listed in the SAMPLING KIT Section of the PW Sampling Procedure.	
II.	DOCUMENTATION INSTRUCTIONS	
	The current date, current time, and your initials have been written in the appropriate highlighted areas of the labels attached to the sample containers, as indicated in the DOCUMENTATION INSTRUCTIONS Section of the <i>PW Sampling Procedure</i> .	ed
	The current date and time have been written on the COC form in the highlighted areas for each sample; your printed name and signature have been written in the highlighted "Sampler(s)" block on the COC form; and the current date, current time and your signature have been written in the highlighted "Relinquished by:" block on the COC form, as indicated in the DOCUMENTATION INSTRUCTIONS Section of the PW Sampling Procedure.	
	The current date, current time, and your signature have been written on both custody seals in the highlighted areas as indicated in the DOCUMENTATION INSTRUCTIONS Section of the <i>PW Sampling Procedure</i> .	
Ш.	PRE-SAMPLING INSTRUCTIONS	
	The cooler has been set up with double-layered garbage bags and ice as indicated in the PRE-SAMPLING INSTRUCTIONS Section of the <i>PW Sampling Procedure</i> .	
IV.	SAMPLE COLLECTION	
	New, unused gloves were put on when indicated in the SAMPLE COLLECTION Section of the <i>PW Sampling Procedure</i> , and whenever the glove(s) were torn or badly soiled.	0.00
	PW samples were collected as indicated in the SAMPLE COLLECTION Section of the PW Sampling Procedure.	
	The filter was replaced whenever it became clogged, as indicated in the SAMPLE COLLECTION Section of the $PW$ Sampling Procedure.	
V.	SAMPLE PACKING	
	Samples were packed into the cooler with ice and sealed as indicated in the SAMPLE PACKING Section of the <i>PW Sampling Procedure</i> .	
Com	nents/Coordinate Verification:	
Signatu	re Date	
Printed	Name Location ID	



# PRODUCED WATER SAMPLING CHECKLIST REV 01 (with duplicates)

Contact Jessica Vickers at <a href="mailto:Jessica.Vickers@tetratech.com">Jessica.Vickers@tetratech.com</a> or 678-983-6655 (cell).

This document lists the steps covered in the training video, which should be viewed no more than five (preferably within two) days before the day of sampling. Use the *Produced Water Sampling Procedure* to guide you during sampling. Check the boxes on this checklist as you complete each step. When finished, sign and date this checklist at the bottom and include it with the sample shipment. Make sure all highlighted information is filled out.

I.	SAMPLING KIT (Check the box to show that the statement is true.)
	The sampling kit cooler contained all items listed in the SAMPLING KIT Section of the PW Sampling Procedure.
	The pump case contained all items listed in the SAMPLING KIT Section of the PW Sampling Procedure.
II.	DOCUMENTATION INSTRUCTIONS
	The current date, current time, and your initials have been written in the appropriate highlighted areas of the labels attached to the sample containers, as indicated in the DOCUMENTATION INSTRUCTIONS Section of the <i>PW Sampling Procedure</i> .
	The current date and time have been written on the COC form in the highlighted areas for each sample; your printed name and signature have been written in the highlighted "Sampler(s)" block on the COC form; and the current date, current time, and your signature have been written in the highlighted "Relinquished by:" block on the COC form, as indicated in the DOCUMENTATION INSTRUCTIONS Section of the PW Sampling Procedure.
	The current date, current time, and your signature have been written on both custody seals in the highlighted areas as indicated in the DOCUMENTATION INSTRUCTIONS Section of the PW Sampling Procedure.
III.	PRE-SAMPLING INSTRUCTIONS
	The cooler has been set up with double-layered garbage bags and ice as indicated in the PRE-SAMPLING INSTRUCTIONS Section of the <i>PW Sampling Procedure</i> .
IV.	SAMPLE COLLECTION
	New, unused gloves were put on when indicated in the SAMPLE COLLECTION Section of the <i>PW Sampling Procedure</i> , and whenever the glove(s) were torn or badly soiled.
	PW samples were collected as indicated in the SAMPLE COLLECTION Section of the PW Sampling Procedure.
	The filter was replaced whenever it became clogged, as indicated in the SAMPLE COLLECTION Section of the PW Sampling Procedure.
	For the "-DUP" sample, a new unused pair of gloves was put on; the tubing and filter were replaced; and the PW sample procedures were repeated for the containers labeled "-DUP" as indicated in the SAMPLE COLLECTION Section of the PW Sampling Procedure.
V.	SAMPLE PACKING
	Samples were packed into the cooler with ice and sealed as indicated in the SAMPLE PACKING Section of the <i>PW Sampling Procedure</i> .
Com	nents/Coordinate Verification:
Signatu	Date Date
Printed	Name Location ID



# **Attachment 1**

************					
ALS Environmental	Houston, Texas 77099 Phone: 281-530-5656				
Client: Tetra Tech-GA	Project: OOC-Produced Water				
Sample ID: MPWCS-PW-001					
Date: Time:	Collect By:				
Analysis: Dissolved CR6	Preservative: Buffer				
BO Prep'd on: 6/3/2013					
ALS Environmental	Houston, Texas 77099				
Client: Tetra Tech-GA	Phone: 281-530-5656				
Chent: Telm Tech-GA	Project: OOC-Produced Water				
Sample ID: MPWCS-PW-001					
Date: Time:	Collect By:				
Analysis: Dissolved Cyanide	Preservative: NaOH				
BO Prep'd on: 6/3/2013					
ALS Environmental	Houston, Texas 77099 Phone: 281-530-5656				
Client: Tetra Tech-GA	Project: OOC-Produced Wate				
Sample ID: MPWCS-PW-001					
Date:Time:	Collect By:				
Analysis: Dissolved Metals	Preservative: HNO				
BO Prep'd on: 6/3/2013					



Holiand, MI +1 616 399 6070

# **Chain of Custody Form**

Houston, TX +1 281 530 5656 Middletown, PA +1 717 944 5541

Page \_

York, PA +1 717 505 5280

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Note: 1. Any changes must be made in writing once samples and COC Form have been submitted to ALS Environmental.

2. Unless otherwise agreed in a formal contract, services provided by ALS Environmental are expressly limited to the terms and conditions stated on the reverse,

3. The Chain of Custody is a legal document. All information must be completed accurately.

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#### APPENDIX B

# **TABLES**

(Five Pages)

# **TABLE**

- 1 SAMPLING LOCATIONS, ANALYSES, AND RATIONALE
- 2 QUALITY ASSURANCE/QUALITY CONTROL SAMPLES
- 3 WATER BASED MUD SAMPLE LOCATIONS
- 4 PRODUCED WATER SAMPLE LOCATIONS
- 5 ANALYTICAL METHODOLOGY, REQUIRED SAMPLE CONTAINERS, AND PRESERVATIVES



# TABLE 1 SAMPLING LOCATIONS, ANALYSES, AND RATIONALE

Sample ID	Sample Type	Analyses	Sample Location	Rationale				
MPWCS-PW-001 through MPWCS-PW-250	Produced Water	Dissolved Metals (As, Cd, Cu, Pb, Hg, Ni, Se, Ag, and Zi), CN, and Cr <sup>+6</sup>	To be determined as discussed in Section 3.0 of the SAP.	To characterize produced water discharges and provide data to support a reasonable potential analysis based on AWQC				
MPWCS-WBM-001 through MPWCS-WBM-250	Water Based Mud	Dissolved and Total Metals (As, Cd, Cu, Pb, Hg, Ni, Se, Ag, and Zi), CN, and Cr <sup>+6</sup>	To be determined as discussed in Section 3.0 of the SAP.	To characterize water based mud discharges and provide data to support a reasonable potential analysis				

#### Notes:

Ag Silver

As Arsenic
AWQC Ambient Water Quality Criteria

Cd Cadmium
CN Cyanide

Cr<sup>+6</sup> Hexavalent chromium

Cu Copper Hg Mercury ID Identification

MPWCS Mud and Produced Water Characterization Study

Ni Nickel Pb Lead

PW Produced water

SAP Sampling and Analysis Plan

Se Selenium

WBM Water based mud

Zi Zinc



# TABLE 2 QUALITY ASSURANCE/QUALITY CONTROL SAMPLES

Sample ID	Sample Type	Rationale
MPWCS-PW-###	MS/MSD	Determine the effect of each sample matrix on the sample preparation procedures and measurement methodology. One
MPWCS-WBM-###	IVIS/IVISD	MS/MSD sample will be designated for every 20 samples collected per media.
MPWCS-PW-###-DUP	Field duplicates	Measure both field and laboratory precision. One duplicate sample will be collected for every 20 samples collected per
MPWCS-WBM-###-DUP	Field duplicates	media.

Notes:

##

Sample number to be determined in the field

DUP

Field duplicate

ID

Identification

MPWCS

Mud and Produced Water Characterization Study

MS/MSD

Matrix spike/matrix spike duplicate

PW

Produced water

WBM

Water based mud

TABLE 3
WATER BASED MUD SAMPLE LOCATIONS

Surface Area Code	Surface Area Label	Total Wells Drilled 2009-2012	Estimated Sample Number <sup>1</sup>
AT	ATWATER * 60.	1	1
EW	EWING BANK 60.	1	1
LL	LLOYD 60.	1	1
MU	MUSTANG ISLAND AREA 42.	1	1
DC	DESOTO CANYON 60.	2	2
EB	EAST BREAKS 60.	2	2
BA	BRAZOS AREA 42.	3	3
MI	MATAGORDA ISLAND AREA 42.	3	3
PL	SOUTH PELTO AREA 17.	3	3
SP	SOUTH PASS AREA 17.	4	4
MO	MOBILE 60.	6	6
SM	SOUTH MARSH ISLAND AREA 17.	8	8
AC	ALAMINOS CANYON 60.	9	9
VK	VIOSCA KNOLL 60.	9	9
WC	WEST CAMERON AREA 17.	10	10
EC	EAST CAMERON AREA 17.	11	10
Ш	HIGH ISLAND AREA 42.	11	10
BM	BAY MARCHAND AREA 17.	12	10
VR	VERMILION AREA 17.	14	10
GI	GRAND ISLE AREA 17.	15	10
KC	KEATHLEY CANYON 60.	19	10
WD	WEST DELTA AREA 17.	19	10
GB	GARDEN BANKS 60.	27	10
EI	EUGENE ISLAND AREA 17.	42	10
SS	SHIP SHOAL AREA 17.	46	10
ST	SOUTH TIMBALIER AREA 17.	47	10
WR	WALKER RIDGE 60	48	10
GC	GREEN CANYON 60.	75	10
MP	MAIN PASS AREA 17.	86	10
MC	MISSISSIPPI CANYON 60.	89	10
	Total Wells Drilled in 3 Years	624	213
	Target Percent Sampled		34%

Notes:

Actual sample locations will be determined by drilling activities during the study period. These data are for illustration and estimation purposes only.

TABLE 4
PRODUCED WATER SAMPLE LOCATIONS

Surface Area Code	Surface Area Label	Unique Produced Water Outfalls	Target Sample Numbe	
AC	ALAMINOS CANYON 60.	1	1	
PN	NORTH PADRE ISLAND AREA 42.	1	1	
BS	BRETON SOUND AREA 17.	2	2	
. CA	CHANDELEUR AREA 17.	3	3	
SA	SABINE PASS (LOUISIANA) 17.	5	5	
EW	EWING BANK 60.	6	6	
GB	GARDEN BANKS 60.	8	8	
PL	SOUTH PELTO AREA 17.	8	8	
VK	VIOSCA KNOLL 60.	8	8	
EB	EAST BREAKS 60.	9	9	
GC	GREEN CANYON 60.	13	10	
BA	BRAZOS AREA 42.	14	10	
GA	GALVESTON AREA 42.	14	10	
MU	MUSTANG ISLAND AREA 42.	14	10	
MC	MISSISSIPPI CANYON 60.	15	10	
GI	GRAND ISLE AREA 17.	17	10	
MI	MATAGORDA ISLAND AREA 42.	21	10	
WD	WEST DELTA AREA 17.	21	10	
SP	SOUTH PASS AREA 17.	23	10	
EC	EAST CAMERON AREA 17.	33	10	
MP	MAIN PASS AREA 17.	46	10	
ST	SOUTH TIMBALIER AREA 17.	47	10	
SM	SOUTH MARSH ISLAND AREA 17.	52	10	
VR	VERMILION AREA 17.	59	10	
SS	SHIP SHOAL AREA 17.	68	10	
WC	WEST CAMERON AREA 17.	77	10	
HI	HIGH ISLAND AREA 42.	85	10	
EI	EUGENE ISLAND AREA 17.	88	10	
	Total Outfalls	758	231	
	Percent Active Outfalls Sampled		30%	

# ${\bf TABLE~5}$ ANALYTICAL METHODS, REQUIRED SAMPLE CONTAINERS, AND PRESERVATIVES

ANALYTICAL PARAMETER	MATRIX	ANALYTICAL METHOD <sup>1</sup>	NUMBER <sup>2</sup> AND TYPE OF SAMPLE CONTAINER	PRESERVATION METHOD	SAMPLE HOLDING TIME
X	No.	WATE	R BASED MUD SAMPLES		
Total and dissolved metals (arsenic, cadmium, copper, lead, mercury, nickel, selenium, silver, and zinc)	Water	SW-846 Method 6020A/7470A and 7471B (mercury)	Two 1-liter polyethylene jars	Cool to 4°C	28 days for mercury and 6 months for all other metals
Total and dissolved cyanide	Based Mud	SW-846 Method 9014		AND	14 days
Total and dissolved hexavalent chromium		SW-846 Method 7196A		1 4	24 hours - not to exceed 48 hours
		PROD	UCED WATER SAMPLES		
Dissolved metals (arsenic, cadmium, copper, lead, mercury, nickel, selenium, silver, and zinc)	Produced	SW-846 Method 6020A/7470A (mercury)	One 500-milliliter polyethylene bottle	Nitric acid to pH<2; cool to 4°C	28 days for mercury and 6 months for all other metals
Dissolved cyanide	Water	SW-846 Method 9014	One 250-milliliter polyethylene bottle	Sodium hydroxide to pH>12; cool to 4°C	14 days
Dissolved hexavalent chromium		EPA Method 218.6	One 250-milliliter polyethylene bottle	Ammonium sulfate buffer solution; cool to 4°C	14 days

Notes:

EPA Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), located at http://www.epa.gov/SW-846/sw846.htm

EPA Method 218.6: Determination of Dissolved Hexavalent Chromium in Drinking Water, Groundwater, and Industrial Wastewater Effluents by Ion

Chromatography, located at http://www.wcaslab.com/tech/218\_6.pdf

For samples designated for matrix spike and matrix spike duplicate (MS/MSD) analysis, double volumes will be collected.

°C Degrees Celsius

< Less than

> Greater than



### APPENDIX C

## **QUALITY ASSURANCE PROJECT PLAN**

(Thirteen Pages)



#### QUALITY ASSURANCE PROJECT PLAN (SHORT FORM)

# MUD AND PRODUCED WATER CHARACTERIZATION STUDY (MPWCS) TO MEET REQUIREMENTS OF THE NATIONAL POLLUTANT DISCHARGE ELIMINATION SYSTEM (NPDES) PERMIT

# WESTERN AND CENTRAL GULF OF MEXICO OUTER CONTINENTAL SHELF (OCS) NPDES PERMIT No.: GMG290000

#### Prepared for

#### OFFSHORE OPERATORS COMMITTEE (OOC) ENVIRONMENTAL SUBCOMMITTEE

Revision 01: March 2014

Date Prepared:

OOC Point of Contact:

Telephone No.:

Prepared by:

Tetra Tech Project Manager:

Telephone No.:

June 5, 2013

Robert Kuehn

(504) 425-7693

Tetra Tech, Inc.

June Mire, Ph.D.

(504) 273-9186

Prepared by Jessica Vickers Tetra Tech Chemist Reviewed by Jim Collins

Tetra Tech Task Manager

Reviewed by John Schendel

Tetra Tech Quality Assurance Officer

Approved by June Mire, Ph.D.

Tetra Tech Project Manager

Approved by Min Huang

OOC Analytical Subteam Lead

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### **ATTACHMENTS**

## Attachment

1 LABORATORY DETECTION LIMITS



dy (MPWCS) to Meet Requirements of the tional Pollutant Discharge Elimination	Location: Western and Central Gulf of Mexico Outer Continental Shelf (OCS)		
Tetra Tech, Inc. (Tetra Tech)	<b>Date:</b> June 24, 2013		
June Mire Date: 06/24/13 Tetra Tech Project Manager	Approved By: Jim Collins Date: 6/24/13 Title: Tetra Tech Task Leader		
Jessica Vickers Date: 06/24/13 Tetra Tech Chemist	Approved By: Robert Kuehn Date: 6/24/13  Title: JIP Core Team Lead, Environmental Subcommittee		
1.0 PROJECT	INFORMATION		
on List:			
Protection Agency (EPA) Region 6:	Tetra Tech:		
ators Committee (OOC):	June Mire Jim Collins Jessica Vickers Randy Bassett		
	June Mire Date: 06/24/13 Tetra Tech Project Manager  Jessica Vickers Date: 06/24/13 Tetra Tech Chemist  1.0 PROJECT on List: Protection Agency (EPA) Region 6:		

#### 1.2 Project/Task Organization:

Kitty Kong Ileana Rhodes

James Fajt Lowell McLeroy

Robert Kuehn will serve as the OOC point of contact for the activities described in this quality assurance project plan (QAPP). June Mire of Tetra Tech will serve as the Tetra Tech project manager and is responsible for maintaining an approved version of this QAPP. Jessica Vickers of Tetra Tech will serve as the Tetra Tech project chemist and is responsible for providing Tetra Tech approval of this QAPP. Additional specific Tetra Tech personnel will be determined prior to initiation of the work described herein.

Len Nelms

John Schendel

#### 1.3 Problem Definition/Background:

Tetra Tech has been contracted to conduct a MPWCS to meet the requirements of NPDES Permit GMG290000 for the Western and Central Gulf of Mexico OCS area. The purpose of the MPWCS is to meet EPA permit requirements that include a characterization study of water based mud (WBM) and produced water (PW) for the express purpose of having "more area-specific data for future evaluations;" and to collect data to characterize representative discharges from wells in the OCS area.



### 1.4 Project/Task Description:

To achieve the objectives of the MPWCS, Tetra Tech will conduct activities for the MPWCS, including the following:

- Identify sample locations using a geographic information system and a hierarchical optimization system.
- Stratify produced water sample locations so the data set will be representative of overall offshore
  production.
- Collect samples to determine the soluble concentration of selected analytes in WBM and PW.

Table 1 in Appendix B of the Sampling and Analysis Plan (SAP) provides details regarding the numbers, types, analytical suite, and locations of all samples proposed. Analytical data will be used to characterize representative discharges from the wells within the OCS area.

#### 1.5 Quality Objectives and Criteria for Measurement Data:

DQOs were established for the OCS to define the quantity and quality of the data to be collected to support the objectives of the MPWCS. DQOs were developed using the seven-step process outlined in the following EPA guidance documents: "EPA Requirements for Quality Assurance Project Plans," EPA QA/R-5, March 2001; "Guidance for Quality Assurance Project Plans," EPA QA/G-5; and "Guidance on Systematic Planning Using the Data Quality Objectives Process," EPA QA/G-4, February 2006.

Q				
Step 1:	Stakeholders: EPA, the OOC, and the affected shoreline communities			
State the Problem	Site History/Conceptual Site Model: See Section 2.0 of the SAP to which this QAPP is appended.			
	<b>Statement of Problem:</b> Sampling and laboratory analysis will be required to provide more upto-date information for refinement of the NPDES permit, and to characterize representative discharges from the wells in the OCS area.			
Step 2: Identify the Goals of	Study Questions: Are dissolved phase contaminants of concern present in the WBM and PW at concentrations that exceed the comparison criteria?			
the Study	<b>Decision Statements:</b> Evaluate analytical data from WBM and PW samples to determine whether contaminant concentrations are present above the comparison criteria.			
Step 3: Identify Information Inputs	Inputs: Analytical results for the WBM and PW samples that will be collected, as well as representative salinity information that will be provided by OOC members, for the sites sampled.			
Step 4: Define Study Boundaries	Spatial Boundary: The OCS area is that part of the continental shelf seaward of the line that marks State ownership along the southern boundary of the United States. It extends along the coastline from Alabama to the Texas, a distance of approximately 630 miles, and extends more than 200 miles offshore (National Oceanic and Atmospheric Administration [NOAA], Google Earth).			
	<b>Temporal Boundaries:</b> Sampling activities are scheduled to commence in Summer 2013. The temporal boundaries for sampling activities extend from when sampling activities are initiated until the OOC declares sampling activities complete.			



Step 5: Develop the Analytical Approach	<ul> <li>Analytical Methods: Table 4 included in Appendix B of the SAP provides details regarding the analytical methodology for the MPWCS activities, including sample containers, preservatives, and holding times. Samples will be analyzed by the ALS Group, Inc. (ALS) laboratory in Houston, Texas, the Tetra Tech-procured subcontract laboratory. The following list summarizes analytical methods that will be used:</li> <li>Select dissolved and total metals (arsenic, cadmium, copper, lead, nickel, selenium, silver, and zinc) will be analyzed by EPA Test Methods for Evaluating Solid Waste, Fourth Edition, Including Updated, I through IVB, February 2007 (SW-846) Method 6020A.</li> <li>Dissolved mercury will be analyzed by SW-846 Method 7470A; total mercury will be analyzed by Method 7471A (in WBM samples).</li> <li>Dissolved cyanide will be analyzed by SW-846 Method 9014; total cyanide will be analyzed by Method 9014 (in WBM samples).</li> <li>Dissolved hexavalent chromium will be analyzed by SW-846 7196A; total hexavalent chromium will be analyzed by EPA Method 218.6 (for PW samples).</li> <li>Dissolved hexavalent chromium will be analyzed by EPA Method 218.6 (for PW samples).</li> <li>The laboratory reporting limits for the analyses to be performed are listed in Attachment 1.</li> <li>Comparison Criteria: Analytical results will be compared with the EPA Ambient Water Quality Criteria for saltwater: <a href="http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm#appendxa">http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm#appendxa</a></li> <li>Decision Rules: Analytical results will be provided to EPA for inclusion in a Reasonable Potential Analysis.</li> </ul>
Step 6: Specify Performance or Acceptance Criteria	Tetra Tech will assess the analytical results for initial acceptance during a Stage 4 validation of the samples that will determine the usability of the data. Any rejected data and the reasons for rejection will be summarized in the data quality assessment report. See Attachment 2.
Step 7: Develop the Plan for Obtaining Data	Optimized Design: Table 1 in Appendix B of the SAP details the samples proposed for collection.
1.6 Special Training/Ce	ertification Requirements:
OSHA 29 CFR 1910	0.0 Special Equipment/Instrument Operator (describe below):  Other (describe below):
Special Requirements:	The personnel who currently collect samples under the NPDES monitoring programs on the individual rigs and platforms selected for sampling will collect the WBM and PW samples. By having the platform personnel, who have already had all relevant training/certification required to work on the rig/platform, collect the samples, Tetra Tech will be able to avoid having to train additional personnel or procure subcontractors with the appropriate training. The personnel on the rigs/platforms will receive training on the sampling procedures via a training video that will be made available to them prior to sampling. The Sampling Procedures Reference Checklists (see Appendix A of the SAP) will be emailed to the platform personnel prior to sampling, and the Tetra Tech chemist will set up a pre-sampling conference with the operator to verify that the training video has been viewed and to review the procedures. If the platform personnel have access to a phone during sampling, the Tetra Tech chemist will be available to address any questions that may arise during sampling. If phone contact during sampling is not available, the platform personnel will call the Tetra Tech chemist as soon as reasonably possible after sampling to debrief on the sample collection.



1.7 Documentation and Records:					
The most current version of this QAPP will be distributed to the entire distribution list presented in Section 1.1. The Tetra Tech project manager will be responsible for maintaining the most current revision of this QAPP and for distributing it to all personnel and parties involved in the field effort. Field records that may be generated include the following:					
	ference Checklists				
☐ Field Instrument Calibration Logs ☐ Photographs					
☐ Field Monitoring and Screening Results ☐ Site Logbook	. *				
☐ Well Logs ☐ Site Maps and Drawings	s				
Field documentation and records will be generated and maintained in accordance with the requirements presented in the Sampling Procedures Reference Checklists, located in Appendix A of the SAP. All field-generated data will also be maintained in the project file and included, as appropriate, in project deliverables in final form after all reviews and applicable corrective actions.					
Laboratory analytical data will be generated and maintained in accordance with the associated analytical methods. A 15-business day turnaround time will be requested for ALS to submit final results to Tetra Tech.					
A summary of field activities, findings and laboratory analytical results will be included in the final MPWCS report. All project records under Tetra Tech's control will be maintained and retained in accordance with Section 4.0 of the Tetra Tech Quality Management Plan (QMP).					

#### 2.0 DATA GENERATION AND ACQUISITION

#### 2.1 Sampling Process Design:

Table 1 in Appendix B of the SAP present details on the types and numbers of samples to be collected, sample locations, sample matrices, and laboratory analytical methods. The rationale for this sampling process design is based on the DQO process discussed in Section 1.5 of this QAPP. Samples will be submitted to ALS for analyses of selected dissolved metals, dissolved cyanide, and dissolved hexavalent chromium.

### 2.2 Sample Methods Requirements:

Matrix	Sampling Method	EPA and Tetra Tech Standard Operating Procedures and Guidance	
WBM	Refer to Table 1 in Appendix B of the SAP for more details,	Refer to the Sampling Procedures Reference	
PW	including requested laboratory analyses and methods.	Checklists located in Appendix A of the SAP.	

Other Sample Method Requirements: The Tetra Tech project manager, in coordination with the Tetra Tech chemist, will be responsible for identifying failures in sampling and field measurement systems, overseeing any corrective actions, ensuring that the corrective actions are documented in appropriate records, and assessing the effectiveness of corrective actions. Equipment required for this sampling in detailed in the Sampling Procedures Reference Checklists located in Appendix A of the SAP.



#### 2.3 Sample Handling and Custody Requirements:

Sample handling and chain-of-custody record keeping will be conducted in accordance with the Sampling Procedures Reference Sheets, located in Appendix A of the SAP. Once collected, samples will be placed on ice and kept in a custody-sealed cooler until the cooler can be transported to shore and shipped to ALS. The Tetra Tech chemist will coordinate with the sampling personnel on the rigs/platforms to ensure that custody of samples is maintained until they are shipped to the laboratory. Close coordination with the sampling personnel will focus on delivering WBM samples to the lab within the allowable 48-hr holding time for dissolved hexavalent chromium. Chain-of-custody records will be used to document the samples collected and delivered to the laboratory.

#### 2.4 Analytical Method Requirements:

The analytical parameters and associated laboratory analytical methods that will be used for this project are listed in Table 1 of Appendix B of the SAP.

A 15-business day turnaround time will be requested for ALS to submit final results to Tetra Tech. Data validation of the analytical data packages will be conducted by Tetra Tech. A Stage 4 data validation will be conducted in accordance with the EPA National Functional Guidelines (NFGs) for Inorganic Superfund Data Review, EPA540-R-10-011, January 2010; as well as the associated analytical methods. Laboratory instruments required for sample analyses are contained in the associated methods.

The data packages will be reviewed to determine whether any data should be rejected and whether any data qualifiers assigned during the validation process affect the usability of the data as defined in Section 1.5 of this QAPP.

#### 2.5 Quality Control Requirements:

QC requirements for laboratory analyses are presented in the EPA NFGs for Inorganic Superfund Data Review, EPA540-R-10-011, January 2010; as well as the associated analytical methods. Method detection limits and reporting limits are included in Attachment 1.

Laboratory and QC samples will include the collection of matrix spike and matrix spike duplicate (MS/MSD) sample sets at a frequency of one MS/MSD set for every 20 samples per medium collected. Field QC samples will include field duplicate samples collected at a frequency of one field duplicate sample for every 20 samples per medium collected. QC samples will be submitted for analyses listed in Table 2 of Appendix B of the SAP.

### 2.6 Instrument/Equipment Testing, Inspection, and Maintenance Requirements:

Laboratory instrument testing, inspection, and maintenance requirements are contained in the associated analytical methods; as well as in the associated manufacturer's operating manuals.

#### 2.7 Instrument Calibration and Frequency:

Instrument calibration and frequency requirements for analytical methods are specified in EPA NFGs for Inorganic Superfund Data Review, EPA540-R-10-011, January 2010; as well as the associated analytical methods.

#### 2.8 Inspection/Acceptance Requirements for Supplies and Consumables:

Supplies and consumables required for this sampling event will be inspected and accepted by the Tetra Tech chemist or designated team member, and the items listed in the Sampling Procedures Reference Checklists, located in Appendix A of the SAP. All sample containers will meet EPA criteria for cleaning procedures for low-level chemical analysis. Sample containers will have certifications provided by the manufacturer in accordance with pre-cleaning criteria established by EPA.



#### 2.9 Non-Direct Measurement Requirements:

Information pertaining to the site (including photographs, maps, and so forth) has been compiled from file information obtained from EPA, NOAA, Google Earth, and the OOC. The extent to which these data and information, if any, are used to achieve the objectives of this project will be determined by Tetra Tech in cooperation with the OOC. Any justifications and qualifications required for the use of these data and information will be provided in the reports generated for this project.

#### 2.10 Data Management:

All reference materials generated during this study and included in the final MPWCS report will be submitted to EPA in portable document format on compact disc. All field-generated data will be managed as part of the permanent field record for the project. All laboratory analytical data will be managed in accordance with the requirements of the associated analytical methods; as well as applicable federal regulations. Finally, all field-generated data and other records generated or obtained during this project will be managed according to the requirements of Section 5.0 of the Tetra Tech QMP.

#### 3.0 ASSESSMENT AND OVERSIGHT

#### 3.1 Assessment and Response Actions:

A laboratory audit may be performed for the analyses that ALS will be performing for this project. This audit will be performed by the Tetra Tech chemist, Jessica Vickers, or appropriate designee. All deliverables that Tetra Tech contributes to in whole or in part, including the final MPWCS report, will be subjected to the corporate three-tiered review process, which includes a technical review, an editorial review, and a QC review, with each reviewer signing off on a QC review sheet when any issues or revisions have been addressed. These audits and reviews will be performed by qualified individuals in accordance with the requirements of Section 9.0 of the Tetra Tech QMP.

#### 3.2 Corrective Action:

The Tetra Tech project manager, in coordination with the Tetra Tech chemist, will be responsible for identifying failures in sampling and field measurement systems, overseeing any corrective actions, ensuring that the corrective actions are documented in appropriate records, and assessing the effectiveness of corrective actions. Corrective action requirements for analytical methods are presented in the associated analytical methods, as well as Section 9.4 of the Tetra Tech OMP.

#### 3.3 Reports to Management:

All formal deliverables to EPA associated with this project will be prepared, reviewed, and distributed in accordance with the requirements of the Section 9.4 of the Tetra Tech QMP, and under the supervision of the Tetra Tech chemist, Jessica Vickers, or appropriate designee.



#### 4.0 DATA VALIDATION AND USABILITY

#### 4.1 Data Review, Verification, and Validation Requirements:

All field-generated data and records (such as the sampling procedures checklists) will be reviewed for completeness and accuracy by the Tetra Tech chemist. These records will be reviewed upon completion of the sampling so that corrective actions, if necessary, can be made prior to transporting the samples to shore.

Data validation of the analytical data packages will be conducted by Tetra Tech. A Stage 4 data validation will be conducted in accordance with the EPA NFGs for Inorganic Superfund Data Review, EPA540-R-10/011, January 2010; as well as the associated analytical methods. The data packages will also be reviewed to determine whether any data are rejected and whether any data qualifiers assigned during the validation process affect the usability of the data as defined in Section 1.5 of this QAPP.

#### 4.2 Verification and Validation Methods:

All field-generated data will be maintained in the project file and included (as appropriate) in project deliverables in final form after all reviews and associated corrective actions. The laboratory analytical data will be validated by Tetra Tech in accordance with the analytical data validation methods provided in the EPA NFGs for Inorganic Superfund Data Review, EPA540-R-10-011, January 2010; as well as the associated analytical methods. The validated analytical data packages will contain a summary of all data qualifier flags and their explanations.

#### 4.3 Reconciliation of the Data to the Project-Specific DQOs:

The Tetra Tech project manager, in cooperation with the OOC, EPA, and the Tetra Tech chemist, will be responsible for reconciling the data and other project results with the requirements specified in this QAPP and by the data users and decision makers. Ultimate acceptance of the data is at the discretion of the EPA and the OOC. Depending on how specific data quality indicators do not meet the project's requirements, the data may be discarded, and resampling and reanalysis of the subject samples may be required. Resampling, reanalysis, or other out-of-scope actions identified to address data quality deficiencies and data gaps will require approval by the EPA and the OOC.

Limitations of the data and data rejection and qualification will be identified during the validation process conducted by Tetra Tech. The data will be reviewed to determine whether any data are rejected and whether any data qualifiers or limitations assigned during the validation process affect the usability of the data as defined in Section 1.5 of this QAPP. All final laboratory data packages will be reviewed to evaluate whether the site-specific DQOs, as defined in Section 1.5 of this QAPP, are met. The data will be reconciled with the project-specific DQOs also in accordance with EPA guidance documents, including "Guidance on Systematic Planning Using the Data Quality Objectives Process," EPA QA/G-4, February 2006.



# ATTACHMENT 1 LABORATORY DETECTION LIMITS

(One Page)



### LABORATORY DETECTION LIMITS

ANALYTE (WBM aqueous phase and PW)	METHOD	METHOD DETECTION LIMIT (mg/L)	REPORTING LIMIT (mg/L) <sup>1</sup>	Saltwater Chronic AWQC (mg/L)	Saltwater Acute AWQC (mg/L)
Dissolved arsenic	SW-846 6020A	0.001	0.005	0.036	0.069
Dissolved cadmium	SW-846 6020A	0.0008	0.002	0.0088	0.04
Dissolved copper	SW-846 6020A	0.001	0.005	0.0031	0.0048
Dissolved lead	SW-846 6020A	0.0007	0.005	0.0081	0.21
Dissolved nickel	SW-846 6020A	0.001	0.005	0.0082	0.074
Dissolved selenium	SW-846 6020A	0.001	0.005	nd	nd
Dissolved silver	SW-846 6020A	0.0008	0.005	nd	0.0019
Dissolved zinc	SW-846 6020A	0.0025	0.005	0.081	0.09
Dissolved mercury	SW-846 7470A	0.000042	0.0002	0.00094	0.0018
Dissolved cyanide <sup>2</sup>	SW-846 9014	0.003	0.02	0,001	0.001
Dissolved hexavalent chromium (WBM)	SW-846 7196A	0.006	0.01	0.05	1.1
Dissolved hexavalent chromium (PW)	EPA 218.6	0.003	0.01	0.05	1.1

Dissolved hexavatent cin simum (1 11)	13171 210.0	0.005	0.01	
ANALYTE (WBM solid phase)	METHOD	METHOD DETECTION LIMIT (mg/kg)	REPORTING LIMIT (mg/kg) <sup>1</sup>	
Total arsenic	SW-846 6020A	0.1	0.5	
Total cadmium	SW-846 6020A	0.05	0.5	
Total copper	SW-846 6020A	0.1	0.5	
Total lead	SW-846 6020A	0.05	0.5	
Total nickel	SW-846 6020A	0.09	0.5	
Totalselenium	SW-846 6020A	0.18	0.5	
Total silver	SW-846 6020A	0.08	0.5	
Total zinc	SW-846 6020A	0.25	0.5	
Total mercury	SW-846 7471B	0.00047	0.003325	
Total cyanide	SW-846 9014	0.6	2	
Total hexavalent chromium	SW-846 7196A	0.7	2	

SW-846

EPA Test Methods for Evaluating Solid Waste, Physical/Chemical Methods Produced Water

PW WBM

Water based mud



Mud and Produced Water Characterization Study

# ATTACHMENT 2 PERFORMANCE OR ACCEPTANCE CRITERIA

(One Page)



### PERFORMANCE OR ACCEPTANCE CRITERIA

DATA QUALITY MEASUREMENTS				
A	Refer to the Sampling Procedures Reference Checklists in Appendix A of the SAP; SW-846 Methods 6020A, 7470A, 7471A, 7196A, and 9014;			
Accuracy	EPA Method 218.6; and the EPA NFGs.			
Precision	Refer to the Sampling Procedures Reference Checklists in Appendix A of the SAP; SW-846 Methods 6020A, 7470A, 7471A, 7196A, and 9014;			
Precision	EPA Method 218.6; and the EPA NFGs.			
Representativeness	s Refer to the Sampling Procedures Reference Checklists in Appendix A of the SAP.			
	As discussed in Section 3.0 of the SAP, water based mud and produced water samples are scheduled for collection. The Tetra Tech project			
Completeness	manager and Tetra Tech chemist are responsible for determining if the laboratory data collected achieve the level of completeness required to			
	meet the objectives of the project.			
Comparability	Sample and data comparability is expected to be achieved by conducting all field and laboratory work using the same, well-documented, and			
	uniform procedures.			

Notes:

EPA

EPA Method 218.6

Environmental Protection Agency
Determination of Dissolved Hexavalent Chromium in Drinking Water, Groundwater, and Industrial Wastewater Effluents by Ion

EPA NFGs

Chromatography, located at http://www.wcaslab.com/tech/218\_6.pdf
EPA National Functional Guidelines for Inorganic Superfund Data Review, EPA540-R-10/011, January 2010

SAP

Sampling and Analysis Plan

SW-846

EPA Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), located at http://www.epa.gov/SW-846/sw846.htm

### APPENDIX D

WATER BASED MUD CHARACTERIZATION (Seven Pages)



#### SAP Appendix D

#### Alternate Approach for Characterizing Dissolved Metals (Including Cyanide) in Water Based Mud

#### **EXECUTIVE SUMMARY**

All drilling mud samples collected to date are clearly characterized as water based mud, but some samples do not yield adequate water to perform the required analyses for dissolved metals and cyanide. Attempts to dilute the drilling mud and then extract water have raised concerns about the interpretation of the results. The use of alternate methods for separating more water from the water based mud has been studied and rejected. A discussion of the issues with US EPA Region 6 supported a revision of the SAP/QAPP to perform analysis of total metals, hexavalent chromium, and cyanide in each water based mud sample. Samples that yield enough water will be analyzed for dissolved constituents also, on a priority basis.

#### D.1 FUNCTION OF WBM IN DRILLING

Water based drilling muds (also called drilling fluids) are specifically blended to improve safety and yield during drilling while minimizing adverse environmental effects upon discharge. The mud must simultaneously cool, lubricate, and support the weight of the drilling apparatus; stabilize the borehole walls; block movement of mud laterally out of the borehole; balance pressure from the formation; suspend cuttings during drilling; and ultimately carry cuttings out of the borehole (Neff 2010). Water based mud is used during variable stages of drilling wells in the Gulf of Mexico (BOEM 2014).

#### D.2 PHYSICAL CHARACTERISTICS AND CHEMICAL COMPOSITION OF WATER BASED MUD

Water based drilling mud differs from other types of drilling muds that have oil or synthetic fluids as their base. Each water based mud is developed by adding a variety of ingredients to an aqueous base fluid that may be freshwater, marine water, or concentrated brine.

#### D.3. INTENTIONAL LACK OF FREE WATER IN WBM

The physical and chemical properties of additives that promote water retention and increase viscosity of water based mud also make it difficult to extract water from the muds. In general, it has been more difficult to separate water from heavier water based muds that are necessary for drilling deeper sections of a well. The proposed modifications to the sampling and analysis protocols were developed in response to samples that were difficult to separate by centrifugation, but will be applied to the remainder of the water based mud samples collected for this study.

#### **D.4 EXTRACTION PROCESSES**

The permit requires that operators measure dissolved metals, hexavalent chromium, and cyanide concentrations in water based mud. These analyses require the following steps: (1) extraction of an aqueous phase out of the water based mud; (2) filtration of the aqueous phase; and (3) analysis of the filtrate. Determinations of metals, hexavalent chromium, and cyanide each require a 50-mL aliquot of aqueous sample.



#### D.4.1 Centrifugation of Whole WBM Sample

As described in the SAP presented to and approved by EPA on July 8, 2013, water based mud samples are centrifuged in the laboratory to extract an aqueous sample for analysis. To date, the laboratory has received and analyzed 31 water based mud samples. About one-third of the water based mud samples yielded an adequate volume of water when centrifuged. Another one-third of the samples required 2x to 5x dilution with deionized water prior to centrifugation before yielding adequate water volume. The final one-third of the water based mud samples required 10x to 40x dilution with deionized water. All samples were soluble in deionized water and eventually yielded adequate water volume when centrifuged, indicating that they met the definition of water based drilling fluid. However, extensive dilution of the water based mud samples has the undesirable consequence of increasing the reporting limits of the analysis, leading to frequent non-detect results above the corresponding screening criteria. Furthermore, it is not known whether dilution of the water based mud sample with deionized water alters the relative dissolved metals concentrations in the extracted water sample.

### D.4.2 Confounding Effects of Centrifugation of WBM after Dilution with Deionized Water

Dilution of the water based mud samples has the undesirable consequence of increasing the reporting limits of the analysis relative to undiluted samples, leading to more frequent non-detect results. The nature of the analysis makes it difficult to overcome this unfortunate confounding feature of dilution.

A second difficulty with the dilution approach is that it is not known whether dilution of the water based mud sample with deionized water alters the relative dissolved metals concentrations in the extracted water sample. To explore this, OOC compared the results of undiluted with diluted extracts from a WBM sample that did yield adequate extract water without dilution: the results showed no consistent pattern or trend across analytes. It could be that dilution with deionized water releases additional metals into the aqueous phase. Conversely, concentrations of some metals may be unaffected by the dilution. More than likely, not all metals respond alike. Furthermore, the complex chemical interactions occurring among the numerous additives in each water based mud sample makes it difficult to examine any potential correlations. Fundamental physio-chemical parameters such as pH, sulfide content, suspended solids, viscosity, redox state, and other characteristics vary among water based mud samples. All of these parameters can influence the solubility of an individual metal and its relative concentration in the aqueous extract.

#### D.4.3. Filter Press: Considered and Rejected

In an attempt to eliminate some of the confounding variables inherent in the dilution approach, the OOC Characterization Study Team investigated using a filter press to extract water from water based mud samples. Mud engineers routinely use a multi-unit filter press (such as the one manufactured by OFI Testing Equipment, Inc. (http://www.ofite.com/products/140-40.asp) to separate aqueous samples from water based mud. The filter press exerts 100 pounds per square inch (psi) of pressure to the mud sample, literally squeezing the water based mud so that even firm gel structures are broken down and water is released. Although this technique has some appealing features, the OOC Characterization Study Team ultimately rejected the approach for the reasons presented below.



The filter press presents the same problem mentioned above for the dilution approach in that it may actually force more metals into the extract than would normally be in the aqueous phase. Because the filter press is not a EPA standardized method for extracting water from water based mud, or even from sediment, a separate validation study would have to be conducted to provide an interpretive context for the results. Moreover, the filter press equipment poses logistical difficulties for quality control. The individual cells and collecting vessels would have to be thoroughly decontaminated between samples. In addition, the filter press does not work quickly; it could take several hours to extract enough water for a single set of analyses. A very large volume of water based mud (about 3 gallons) would have to be collected and pressed, creating a storage and disposal problem for the laboratory. Finally, the filter presses are custom-built to order, and the manufacturer has a waiting period of several weeks. For these reasons, the OOC Characterization Study Team determined that switching the extraction method to the filter press is not technically sound.

#### D.4.4 Revised Approach to Determining Dissolved Metals in Water Based Mud

Based on a meeting with EPA Region 6 personnel on February 25, 2014, the OOC has revised the approach to determining concentrations of dissolved metals in water based mud using standard EPA methods of digestion and analysis for evaluating effluent (see Attachment D-1). OOC will analyze total constituents in water based mud samples using the EPA SW-846 methods listed below:

Analytes	Method	Prep	Equipment	Citation
As, Cd, Cu, Pb, Ni, Se, Ag, Zn	SW6020	SW3050A	ICP-MS	http://www.epa.gov/osw/hazard/te stmethods/sw846/pdfs/6020a.pdf
Hg	SW7471B	SW7471A	cold-vapor atomic absorption	http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/7471b.pdf
CN-	SW9014	SW9010C	titrimetric and manual spectrophotometric	http://www.epa.gov/osw/hazard/te stmethods/sw846/pdfs/9014.pdf
Cr6+	SW7196 A	SW3060A	colorimetric	http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/7196a.pdf

In addition to the analysis of total constituents, WBM samples will be centrifuged and the resulting aqueous sample (if any) will be analyzed for dissolved constituents to the extent practicable. Methods for analyzing dissolved constituents are in Section 5.0 of the SAP. The concentrations of dissolved components may help determine a correlation between dissolved and total concentrations in the drilling mud. If the WBM sample does not yield enough water to analyze all of the metals listed above, the lab will analyze as many metals as possible on each sample, in the following order of priority: metals, hexavalent chromium, cyanide.

Cyanide has been assigned the lowest relative priority because water based drilling muds do not contain any known source of cyanide. Interviews with several mud engineers and experts in the field confirmed that none of the ingredients permitted for addition to water based mud contain cyanide or chemicals that could degrade to cyanide (Dr. Jerry Neff, personal communication). Cyanide is unlikely to occur naturally in offshore marine sediments or drill cuttings. One exception is organically-enriched low-oxygen sediments (and presumably cuttings) in salt marsh environments (Kamyshny et al., 2013 and references within). It is reported that plants, fungi and bacteria rapidly degrade cyanide



in the marine environment; most cyanide in oceanic waters originates from burning of biomass in terrestrial settings (Kamyshny et al., 2013 and references within). In short, no association of cyanide with drilling muds was found in the published literature.

#### **D.4 SUMMARY**

All drilling mud samples collected to date are clearly characterized as water based mud, but many of the samples do not yield adequate water to perform the required analyses for dissolved metals. The initial approach of diluting the water based mud to increase the yield of centrifuged water has raised some concerns and caused the OOC Characterization Study Team to consider a more robust plan for obtaining the data required by the permit. The dilution step of the procedure is being eliminated out of concern that the dilution process may not yield meaningful results due to elevated reporting limits and variability among proprietary recipes of WBM. The use of a filter press was considered and rejected because of numerous concerns about method standardization, decontamination, and other logistical issues. Therefore, as agreed with US EPA in a meeting 2/15/14, this revised SAP/QAPP will analyze total metals, hexavalent chromium, and cyanide in water based mud samples. In cases where adequate volume of water can be obtained from the water based mud samples by centrifugation, dissolved constituents will be analyzed in order of priority: (1) metals; (2) hexavalent chromium; (3) cyanide.

#### **D.4 REFERENCES**

- Boehm, P., D. Turton, A. Raval, D. Caudle, D. French, N. Rabalais, R. Spies, and J. Johnson. 2001. Deepwater Program: Literature Review, Environmental Risks of Chemical Products Used in Gulf of Mexico Deepwater Oil and Gas Operations. New Orleans, LA. I: Technical Report: 325.
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- Kamyshny, A., Jr., H. Oduro, et al. (2013). "Hydrogen Cyanide Accumulation and Transformations in Non-polluted Salt Marsh Sediments." Aquatic Geochemistry 19(2): 97-113.
- Neff, J.M. 2010. Fate and Effects of Water Based drilling Muds and Cuttings in Cold Water Environments. Report to Shell Exploration and Production Company, Houston, Texas. May 25, 2010. 287 pp.
- U.S. EPA. 2012. Final NPDES General Permit for New and Existing Sources and New Dischargers in the Offshore Subcategory of the Oil and Gas Extraction Category for the Western Portion of the Outer Continental Shelf of the Gulf of Mexico (GMG290000). 77 Federal Register No. 196 [October 10, 2012: 61605 61606].



#### **ATTACHMENT D-1**

#### NOTES ON THE TELECONFERENCE WITH EPA REGION VI

#### FEBRUARY 25, 2014

(2 Pages)

A teleconference was held on February 25, 2014 to discuss an alteration in the study plan for the Water Based Mud and Produced Water Characterization Study (the "Study")being carried out by a group of Gulf of Mexico operators to meet their requirements for water based drilling fluid and produced water characterization under NPDES Permit GMG290000. The participants in the call were Taimur Sheikh and Isaac Chen (EPA Region 6), Joseph Smith (ExxonMobil Upstream Research Company, representing the Study participants, June Mire and Len Nelms (both of Tetra Tech Inc., contractor for the Study).

#### Background

NPDES Permit GMG290000 requires analysis of the dissolved concentrations of certain components in water based drilling mud. It has proved to be difficult to get an adequate volume of water from water based drilling mud for analysis of soluble components. This difficulty arises because the muds are formulated to be stable suspensions and to resist filtration so that they can have the desired operational properties.

The study participants and Tetra Tech asked to have a discussion of possible solutions to this problem with EPA Region 6 so that EPA would be informed of the need to change the original study plan.

#### **Discussion Notes**

The study participants and Tetra Tech have considered analyzing the total concentrations of the target analytes in drilling mud (as opposed to the dissolved concentrations) as well as diluting the mud with deionized water or artificial seawater to facilitate obtaining a sample of the dissolved phase of the drilling mud. EPA Region 6 expressed a preference for avoiding dilution. The group acknowledged uncertainties associated with developing equilibrium coefficients for such a large set of variable drilling mud formulations.

It was agreed that the total concentrations of target analytes in drilling mud would be determined using SW 6020. In cases where sufficient water can be extracted from the drilling mud without dilution, the concentrations of dissolved components will be determined to help understand the correlation between dissolved and total concentrations in the drilling mud.

Determination of dissolved concentrations requires separate analyses for metals, hexavalent chromium, and cyanide. It was agreed that in situations where water could be extracted from drilling mud, the water would be used to determine concentrations of hexavalent chromium first, then metals. Cyanide will not be analyzed. The group discussed the wisdom of changing from drilling mud, the water would be used to determine concentrations of hexavalent chromium first,



then metals. Cyanide will not be analyzed. The group discussed the wisdom of changing analytical methods to use instruments that require less water volume, such as gas furnace atomic absorption spectroscopy, but determined that such a change was not warranted.

The occurrence of cyanide in drilling fluid is considered highly unlikely. EPA requested that the operators provide them with information on the use of materials containing cyanide in water based drilling mud.

It was agreed that the results of samples already analyzed using dilution with deionized water would be reported to EPA as a separate data set. Any available residual samples of previously analyzed drilling muds will be subjected to a determination of total concentrations of metals if sufficient sample volume is available.

#### Follow Up After the Teleconference

Follow up conversations with drilling fluid suppliers and a brief search of the literature supported the view that the occurrence of cyanide in drilling fluids was highly unlikely. Discussions with drilling fluid suppliers indicated that materials with cyanide are not deliberately added to drilling fluids. A brief search of the literature failed to turn up any studies that showed the presence of cyanide in drilling fluids.



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